

The oxygen isotope effect in the ab-plane reflectance of underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

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We have measured the effect of oxygen isotope substitution on the ab-plane reflectance of underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The frequency shift of the transverse optic phonons due to the substitution of ^{16}O by ^{18}O yields an isotope effect of the expected magnitude for copper-oxygen stretching modes with $\alpha = 0.5 \pm 0.1$. The reflectance shoulder at $400 - 500 \text{ cm}^{-1}$ shows a much smaller exponent of $\alpha = 0.1 \pm 0.1$ in the normal state and $\alpha = 0.23 \pm 0.1$ in the superconducting state. These observations suggest that the shoulder is of electronic origin and not due to a phonon mode as has been suggested recently.

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The absence of a substantial isotope effect on the transition temperature of high temperature superconductors has been used to rule out phonons as the bosons responsible for coupling between the charge carriers[1]. But this lack of T_c shift with isotope substitution has failed to convince everyone. Many mechanisms in addition to the frequencies of the underlying phonon can affect T_c . For example, among BCS superconductors, there are examples where the isotope effect of T_c is small and even positive due to the Coulomb interaction parameter μ^* [1], whereas we know that the underlying boson frequencies, phonons in this case, would show a square root dependence on isotopic mass. Thus the isotope effect of T_c is of marginal value in settling the question of phonon origin of superconductivity. A direct measurement of the isotope effect of the boson frequency is a much more convincing test.

Recently, attention has been directed to the kink in the dispersion of the angle-resolved photoemission spectra (ARPES)[2, 3, 4, 5]. The simplest picture of the kink is that it is the result of the interaction of the charge carriers with a bosonic excitation. This opens a new scattering channel at the energy required to generate the excitation, and according to Kramers-Kronig relations applied to the complex self energy, a kink is formed in the energy dispersion[2]. In infrared spectroscopy the kink can be seen as an onset of absorption or a "knee" in low temperature reflectance spectra around 500 cm^{-1} , a result of enhanced scattering above this energy[6, 7]. The energy of the knee does not vary among the various high temperature superconductors with the notable exception of the three-layer mercury compound where it is at a substantially higher energy, at 750 cm^{-1} [8].

The knee has been associated with the superconduct-

ing transition (in optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ it can only be seen below T_c), although in most underdoped materials it is present in the normal state and has therefore been related to the pseudogap[6]. This has led to the suggestion that the bosonic excitation responsible for the knee is a possible candidate for the pairing excitation of high temperature superconductivity[9, 10], similar to the role played by phonons in conventional superconductivity. Recently Lanzara *et al.* have proposed that certain zone boundary oxygen vibrations are responsible for the kink in ARPES dispersion curves[9]. A more conventional view is that the excitation is of magnetic origin[10, 11]. Suggestions that it is related to the sharp 41 meV neutron resonance have been challenged recently[12].

An obvious experiment that will distinguish between these two models of the kink excitation is the oxygen isotope effect of the frequency of the kink. If the kink is due to phonons, its frequency should vary as the -0.5 power-law of the reduced mass of the mode. On the other hand, the frequency of a purely magnetic mode should be independent of isotopic mass. Any such experiment will be difficult because the mode giving rise to the kink is broad. This is illustrated in Fig. 1a where we use standard transport theory[13] to calculate the conductivity and the reflectance in a Fermi liquid system coupled to a bosonic mode. We model the kink excitation as a copper-oxygen stretching mode phonon of 12 cm^{-1} width centered at 516 cm^{-1} , interacting with the charge carriers with a plasma frequency $\omega_p = 1.9 \text{ eV}$ and a coupling constant $\lambda = 2.2$. Fig. 1a shows that within this model, the complete replacement of ^{16}O by ^{18}O in the copper oxygen planes, results in the displacement of the knee in reflectance to lower frequency curve by 24 cm^{-1} , or al-

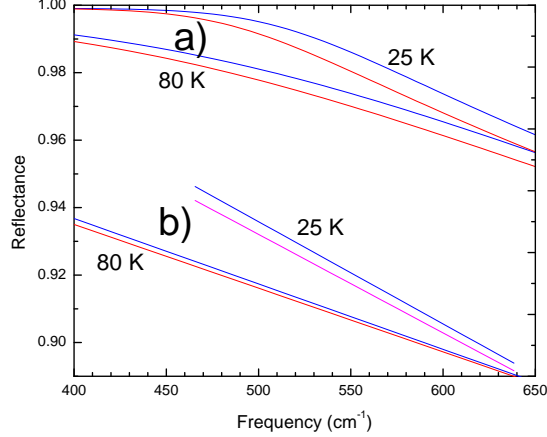


FIG. 1: Top curves (a), model calculation of the reflectance change on oxygen isotope substitution at 25 and 80 K for an copper-oxygen stretching mode phonon at a frequency of 516 cm^{-1} coupled to the charge carriers with $\lambda = 2.2$ and $\omega_p = 1.9$ eV. Bottom curves (b) straight lines fit to reflectance experiments on isotopically separated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. For each temperature, two curves are shown, the top curve (dashed) is for ^{16}O , the bottom one (solid) for ^{18}O .

ternately, a reduction of reflectance in the spectral region above the knee by 0.7 %. We express a partial isotope effect of the frequency of the mode ν in terms of the isotope coefficient α defined in $d\nu/\nu = -\alpha dm/m$ where m is the reduced mass of the copper-oxygen stretching vibration.

To our knowledge, there are no published experiments on the isotope dependence of the frequency scale associated with the pseudogap state or the kink in dispersion of the charge carriers. There are however several reports, based on NMR and NQR measurements, on the isotope dependence of the temperature T^* associated with the onset of the pseudogap in $\text{YBa}_2\text{Cu}_4\text{O}_8$, a material that is naturally underdoped with a $T_c = 80$ K. A zero isotope coefficient was reported by Williams *et al.* [14], whereas Raffa *et al.* [15] found a value of $\alpha = 0.061$ for T^* . The same value, within experimental error, of $\alpha = 0.056$ was found for the superconducting transition temperature T_c , defined as α in $dT_c/T_c = -\alpha dm/m$ where m is the mass of the oxygen isotope. Giant isotope effects have been reported on the relaxation rate of crystal field excitations [16].

For the experiment we used a large single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which was broken in two pieces which were parallel annealed, one in ^{16}O and the other in ^{18}O to yield two underdoped samples. The weight changes of the crystals were consistent with a near complete isotope exchange. Neutron diffraction experiments showed that the occupancy of the chain sites was identical for the two samples. More importantly, the measurements also

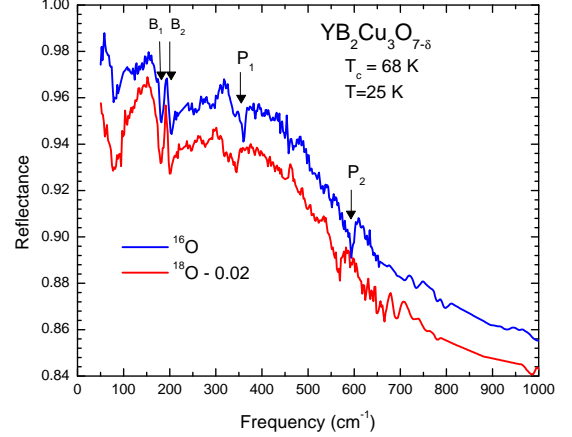


FIG. 2: The reflectance of $\text{YBa}_2\text{Cu}_3^{16}\text{O}_{7-\delta}$, top curve, and isotopically substitute $\text{YBa}_2\text{Cu}_3^{18}\text{O}_{7-\delta}$, lower curve. The frequency shift of two transverse optic phonons, P_1 and P_2 can be seen whereas two electronic excitations, B_1 and B_2 do not shift. For clarity the ^{18}O curve has been shifted down by 0.02.

show that the z -parameter of apical oxygen only shifts by $-0.00003(4)$ c -axis units which is the opposite sign from what one would expect if the shift in T_c was solely due to a difference in oxygen occupation ($+0.00006$) [17]. The uncertainty in the apical oxygen position gives an uncertainty in T_c of 0.45 K. The change in shoulder frequency with T_c is approximately $2.5 \text{ cm}^{-1}/\text{K}$ giving an uncertainty in the shoulder frequency due to occupancy of the chain site of only 1.1 cm^{-1} . This is too small to compensate for a possible isotope shift expected due to phonons (see Fig. 1) of 24 cm^{-1} .

The superconducting transition temperatures were $T_c = 67.6$ K for ^{16}O and $T_c = 66.7$ K for ^{18}O which yields a (partial) isotope coefficient $\alpha = 0.1$. For a pure electron-phonon interaction in a monatomic system, $\alpha = 0.5$. A small value of α is typical of high temperature superconductors [1]. The advantage of an underdoped sample is that it allows us to measure the kink frequency in both the normal and the superconducting state. The samples were twinned.

The reflectance measurements were performed on freshly cleaved faces normal to the c -axis. To correct for irregularities of the surface, resulting from the cleavage process, the sample was coated with a gold layer, evaporated *in situ* [18].

All the measurements were carried out in a cold-finger flow cryostat with a minimum sample temperature of 25 K. A Bruker IFS 66 v/S spectrometer was used in the far-infrared with He-cooled bolometer detectors below 700 cm^{-1} and an MCT detector up to 8000 cm^{-1} . The absolute reflectance measurements have an error of ± 0.5 %.

Figure 2 shows the reflectance of the two crystals at 25 K. Since the spectra are nearly identical on the scale of the figure, the ^{18}O curve has been displaced downward by 0.02 for clarity. We have normalized the two spectra in the 250 to 420 cm^{-1} region, below the reflectance shoulder frequency, by subtracting 0.3 % from the reflectance of the ^{16}O curve at 25 K and 0.75 % at 80 K.

In Fig. 2 the reflectance minima marked P_1 (bond bending) and P_2 (bond stretching) are due to transverse optic phonons[19]. The effect of the isotopic substitution on their resonant frequencies can be seen clearly. From the isotopic masses one expects a frequency ratio (FR) $\nu_{18}/\nu_{16} = 0.9428$ for pure copper-oxygen stretching vibrations. The observed values of FR at 25 K are 0.956 and 0.953 for P_1 and P_2 respectively. The expected values from the shell model of Chaplot *et al.*[20] are 0.954 and 0.9456 respectively. The zone boundary half breathing mode is predicted to have an isotope ratio of 0.9437, close to the pure oxygen vibration. Note, however, that the anomalously low frequency of the half-breathing mode is not correctly described by the model. The good agreement of FR with the theoretical values is consistent with complete in-plane isotopic substitution since the isotope effect on phonon frequencies is reduced for isotopic mixtures in a linear fashion[21].

The modes marked B_1 and B_2 do not shift significantly with isotopic substitution. Their frequencies and spectral weights suggest that they may be related to the modes discussed recently by Bernhard *et al.*[22]. These authors found two modes in this spectral region with spectral weights over an order of magnitude larger than what is expected for phonons, and suggested that they may be of electronic origin. The absence of an oxygen isotope shift supports this picture although, it should be pointed out, low frequency modes generally involve heavier atoms in the unit cell and would not be expected to exhibit a complete oxygen isotope shift. While the modes B_1 and B_2 have been seen by previous workers[22], they were not seen in ultra-pure crystals[23] and are likely activated by impurities.

We obtained the frequency shift of the shoulder with isotope substitution in several ways. The most straightforward method would be to evaluate the second derivative of the reflectance which is closely related to $\alpha^2 F(\Omega)$ [10, 24, 25, 26, 27] which has a peak at the frequency of the mode responsible for the shoulder in the conventional Fermi liquid picture. We find this peak at 520 cm^{-1} in the superconducting state and at 420 cm^{-1} at 80 K, in the normal state. However, as a recent study shows, even with large crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ which have very flat surfaces, the error of this method is too large to resolve the isotope effect[28]. The source of this error is the well known growth of error with successive differentiation. To find a peak position in the $\alpha^2 F(\Omega)$ spectrum, we must in effect evaluate the zero-crossing of the third derivative of the reflectance.

To achieve the required resolution, we adopted the simpler method of evaluating the shift along the frequency axis of the slope portion of the reflectance in the 480 to 620 cm^{-1} region. As Fig. 1 shows, within the Fermi liquid model, the isotope effect gives rise to a uniform shift of the curves along the frequency axis. We evaluated this shift in three different ways. The simplest was to fit a straight line to the reflectance in the slope region and to evaluate the frequency shift of this line for the two isotopes. This method gave $\alpha = 0.23 \pm 0.1$ in the superconducting state at 25 K and $\alpha = 0.1 \pm 0.1$ in the normal, pseudogap state, at 80 K. To minimize uncertainties in the values of the absolute reflectance, all the curves were normalized in the 250 to 420 cm^{-1} region. In the second method, we again normalized the curves in the flat region and evaluated the average shift in reflectance in the slope region and divided this by the slope of reflectance, $dR/d\omega$ to get the frequency shift. Within an experimental error of α of 0.1, the results were the same as those obtained by the first method.

We were concerned with the influence of the optic phonons P_1 and P_2 to our analysis. The third, more elaborate method, was designed to subtract the optic phonons from the spectra. We started by fitting the normalized reflectance to a series of six Lorentzian oscillators that described the optical conductivity in the 250 to 1000 cm^{-1} region. These included a Drude oscillator and the two phonons. We then recalculated the reflectance, without the phonons, and fitted a straight line in the slope region to the calculated model reflectance. The resulting isotope shift was identical to the one found by a direct fit to the experimental reflectance that included the phonons.

The increased isotope dependence of the shoulder in the superconducting state may be related to the isotope effect of the superconducting transition temperature[1]. In our samples $\alpha(T_c) = 0.1 \pm 0.1$. In several models of the shoulder at 520 cm^{-1} , its frequency in the superconducting state is a sum of the normal state mode frequency and the superconducting gap frequency[10, 27]. If there is a proportionality between the superconducting transition temperature and the gap frequency, we would expect an additional isotope effect of 0.1 in the superconducting state within the scope of these models. This is roughly what we observed.

Another experiment that is difficult to reconcile with the phonon model for the shoulder is the infrared reflectance of the three-layer mercury-based superconductor which has a T_c of 130 K. In this material the shoulder frequency is at 750 cm^{-1} , some 45 % higher than in materials with a maximum T_c in the 94 K region[8]. There are no direct measurements of the oxygen stretch frequency in this material. However, one can estimate this frequency from the general rule $\omega^2 \propto a^{-3}$ where a is the lattice parameter[29, 30]. The lattice parameter of the three-layer mercury compound is 3.854 at optimal

doping, as compared to 3.827 in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The calculated phonon frequency shift, based on the lattice parameter change, is -0.5 %. This is to be compared to the observed shift of the shoulder of +45 %.

In summary, we have measured the effect of substituting the oxygen isotope ^{18}O for ^{16}O on the infrared reflectance spectrum of underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. We find that two peaks, previously assigned to phonons, show the expected isotope shift with a coefficient close to the theoretical value of 0.5, whereas the reflectance shoulder has a much smaller coefficient of 0.1 ± 0.1 in the normal state which increases to 0.23 ± 0.1 in the superconducting state. Thus, within experimental error, we can rule out any simple phonon model involving copper-oxygen stretching modes as an explanation for the reflectance shoulder in the normal state. The small isotope shift of the shoulder suggests that it is largely of electronic origin.

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